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GALLIUM PHOSPHIDE

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PROJECT 5108: A STUDY OF $\text{GaAs}_x\text{P}_{1-x}$

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The object of this project is to evaluate the optical, electrical and metallurgical properties of the $\text{GaAs}_x\text{P}_{1-x}$ alloy. Among evaluations of particular interest to us are the investigation of the crystal structure and its imperfections by the Kossel line technique and by that of the lattice absorption spectra as the mole fraction of GaAs, x , varies from 0 to 1.

In this quarter, we have extended our study into alloy regions containing less than 30 percent P. We have developed a method to obtain controllable low feed rates of Pcl_3 vapor necessary in the process of growing crystals in this region. Spectra of two phonon combination bands were also taken; we could trace the GaP-like band down to the 5 percent P alloy. We were also able to detect two reflectivity maxima in the region of 25μ to 40μ ; they are located near the Reststrahlen bands of pure GaP and GaAs respectively. This does not agree with our previous assumption, made without benefit of spectra from alloys in this region, that the Reststrahlen band shifts continuously from GaP to GaAs.¹

I. CRYSTAL GROWTH

It was pointed out in our last report² that the calculated composition of the crystal deviates from the measured value by as much as 15 percent in composition at the low P end. Our control was inadequate because of the effect of diffusion of Pcl_3 vapor into the system (at 0°C the vapor pressure of Pcl_3 is three times higher than that of Ascl_3 at 25°C) which is enhanced at low flow rates. We have recently mixed Ascl_3 with Pcl_3 in one of the bubblers to lower the vapor pressure of Pcl_3 and have operated at an adequate flow rate.

This method proved to be quite successful. Table I is a brief description of the last two runs made in this quarter. The calculated composition is based on the assumption that the partial vapor pressure of PCl_3 is equal to the mole fraction of PCl_3 times the vapor pressure of the pure material (Henry's law with $\gamma = 1$).

II. LATTICE ABSORPTION SPECTRA

The alloy crystals with low P content are expected to be of great interest. The effect of the superposition of combination bands should be very clear in these samples due to the following reasons: (1) the integrated absorption of pure GaAs in the spectral range of 400 cm^{-1} to 800 cm^{-1} is much lower than that of GaP; (2) the effect of the Reststrahlen band should be negligible; (3) there are bands of pure GaP well separated from those of GaAs at the higher frequency side. We should also be able to detect if indeed the Reststrahlen band shifts continuously from GaP to GaAs, which would require a rather sudden change in this region of the alloy.¹

A. Combination Band

The absorption coefficient versus wave number in the range of 400 cm^{-1} to 800 cm^{-1} of samples No. 28 and No. 29 are given in Figs. 1 and 2. The remarks are given as follows:

1. The bands at 575 cm^{-1} for GaP and 525 cm^{-1} for GaAs have merged at 530 cm^{-1} in sample No. 28 and 528 cm^{-1} in sample No. 29.

2. The new broad band at 610 cm^{-1} reported in our previous work² has broadened and reduced in intensity as the P content is reduced. We believe this broad band is due to the presence of P in the alloy as a minority constituent.

3. The spectra in the range of 400 cm^{-1} to 600 cm^{-1} is similar to that of pure GaAs; particularly so with sample No. 29.

4. The GaP-like bands near 700 cm^{-1} have shifted to 710 cm^{-1} and 706.5 cm^{-1} respectively in the two samples and diminished further in the magnitude of absorption. The fact that we observed an absorption band near 700 cm^{-1} with only 5.4 percent P in the alloy undoubtedly demonstrates a superposition of combination bands of pure materials in the alloyed crystals.

B. Reststrahlen Bands

From the reflectivity spectra of samples No. 28 and No. 29, we find two maxima; one is located near 29μ , the other near 36μ . The latter is about at the position where the Reststrahlen band of pure GaAs is located. We have also re-taken the spectra of sample No. 25² and pure GaAs with a minimum amount of stray light. In Fig. 3, we have shown the reflectivity spectra of various samples (including some of the earlier samples). It is clear that the bands near 29μ for samples No. 28 and No. 29 are just part of the continuous shift of the GaP-like band beginning at 26.4μ . However, we were not able to detect a distinct second peak in samples with more than 30 percent P. This is partly due to the instrumental difficulty of resolving small signals from the noise and from stray light in this end of the spectra. In 1959, Oswald³ studied the system $\text{InAs}_x\text{P}_{1-x}$ and observed that the Reststrahlen bands are rather insensitive to the change of composition in the range of 100-20 percent P and that they all bunched at the longer wavelength side of the band of pure InP at 30μ . But he did not investigate further beyond 35μ , while the Reststrahlen band of InAs ⁴ is at 45μ .

We have plotted in Fig. 4, the Reststrahlen frequency versus composition. From our data, it is reasonable to assume that there are optical modes of phonons in the alloyed crystal corresponding to the vibrations of the P and

As sublattices against the Ga sublattice. For the pure material, the resonance peak corresponds to the creation of single optical phonons at $k \approx 0$ in reciprocal space; the vibration mode is thus of very long wavelength and hence requires long range order in the crystal. In the alloy crystal, such long range order is definitely lacking; the existence of similar resonances could be due to short range order if momentum conservation in the coupling between phonon and photon can be relaxed.

To test this idea, we assume the short range order takes the form of clusters of P or As at the column V sites in the zincblende structure with a unique lattice constant. We shall apply Grüneisen's law⁵ to the pure materials by introducing a small volume change to match the observed lattice constant of the alloy and then compute the shift in the frequency of the vibration mode. We shall compare this with our experimental data given in Fig. 4.

The Grüneisen relation gives:

$$\alpha = \gamma \frac{K}{V} C_v, \quad (1)$$

where γ is the Grüneisen constant given by the relation

$$\gamma = - \frac{\Delta \omega_k}{\omega_k} \bigg/ \frac{\Delta V}{V}. \quad (2)$$

α is the volume expansion coefficient, K is the compressibility, V the volume of one gram atom, C_v the specific heat per gram atom at constant volume, and ω_k is an eigen-frequency of the solid.

In the case of GaP,^{6,7} $\alpha = 15.9 \times 10^{-6} \text{ deg}^{-1}$, $V = 4.13^{-1} \text{ cm}^3 \text{ gm}^{-1}$,
 $C_v = 0.124 \text{ cal-gm}^{-1} \text{-deg}^{-1}$ and $K = 0.77 \times 10^{-12} \text{ dyne-cm}^{-2}$; from Eq. (1) we
 calculate that $\gamma = 0.97$ and from Eq. (2)

$$\frac{\Delta\omega_k}{\omega_k} = -0.97 \frac{\Delta V}{V} = -2.91 \frac{\Delta a}{a_{01}} . \quad (3)$$

In the case of GaAs,⁶ $\alpha = 17.1 \times 10^{-6} \text{ deg}^{-1}$, $V = 5.32^{-1} \text{ cm}^3 \text{ gm}^{-1}$,
 $C_v = 0.086 \text{ cal-gm}^{-1} \text{-deg}^{-1}$ and $K = 1.34 \times 10^{-12} \text{ dyne-cm}^{-2}$; so that

$$\gamma = 0.675$$

and

$$\frac{\Delta\omega_k}{\omega_k} = -0.675 \frac{\Delta V}{V} = 2.02 \frac{\Delta a}{a_{02}} . \quad (4)$$

The dashed lines in Fig. 4 are plots of Eqs. (3) and (4) with
 $.20 \text{ \AA} \geq \Delta a \geq 0$, $a_{01} = 5.45 \text{ \AA}$ for GaP and $a_{02} = 5.65 \text{ \AA}$ for GaAs. The fit is
 exceedingly good.

III. REMARKS

The model described above should also be adequate to explain the combination band we have observed in these alloy crystals, namely the superposition of bands of the pure materials. We shall study this further in the coming quarter. We are also investigating whether the same experimental results can be explained by a model other than that involving clusters in the alloy

crystal.

A paper titled "Lattice Absorption in $\text{GaAs}_{1-x}\text{P}_x$ Single Crystals" will be given by us orally at the American Physical Society Spring Meeting at Kansas City, Missouri on March 27, 1965.

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TABLE I

Run No.		No. 28	No. 29
Substrate (GaAs)	Temperature	805	805
	Temp. Gradient °C/cm	16	16
	Orientation	(111)	(111)
	Angle Against Flow	30°	30°
Flow of H ₂	By Pass cc/min	30	30
	Mixture (0°C) cc/min	19	11
	AsCl ₃ (25°C) cc/min	90	90
Mole Fraction of PCl ₃ in Mixture		0.2	0.1
Calculated Composition %P from Flow Rates		11	3
Growth Time hrs/thickness μ		6.25/450	6.5/450
Lattice Constant Å		5.617	5.642
Composition %P		17.7	5.4
Energy Gap (at α = 10 cm ⁻¹ 300°K) eV		1.57	1.42
Free Carrier Absorption		None	None

FIGURE CAPTIONS

- Fig. 1 Lattice absorption bands of $\text{GaAs}_{0.946}\text{P}_{0.054}$ at 300°K .
- Fig. 2 Lattice absorption bands of $\text{GaAs}_{0.823}\text{P}_{0.177}$ at 300°K .
- Fig. 3 Reflectivity spectra of $\text{GaAs}_x\text{P}_{(1-x)}$ samples in reststrahlen region.
- Fig. 4 Reststrahlen frequency versus composition (width taken 10% off peak).

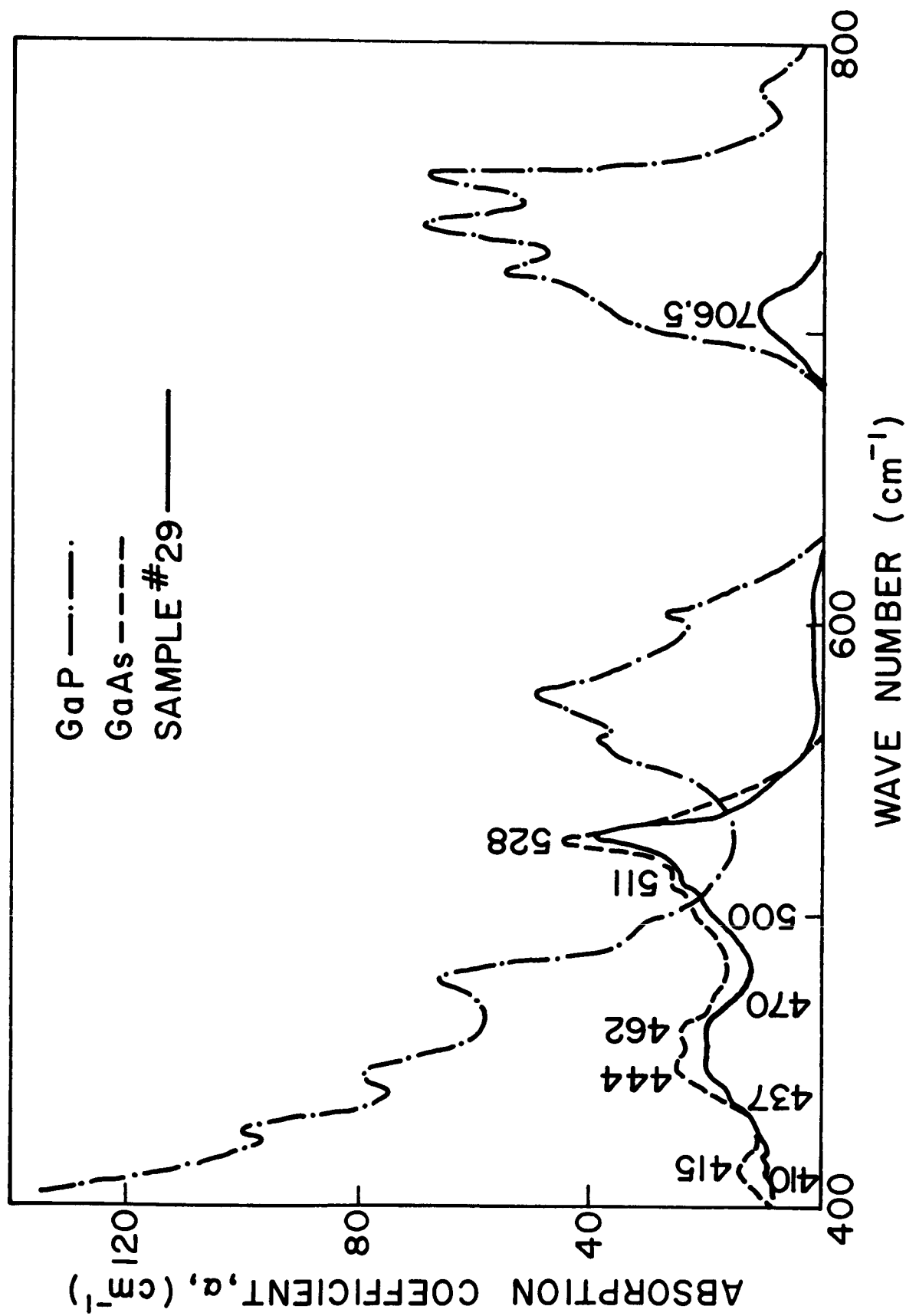


FIG. 1

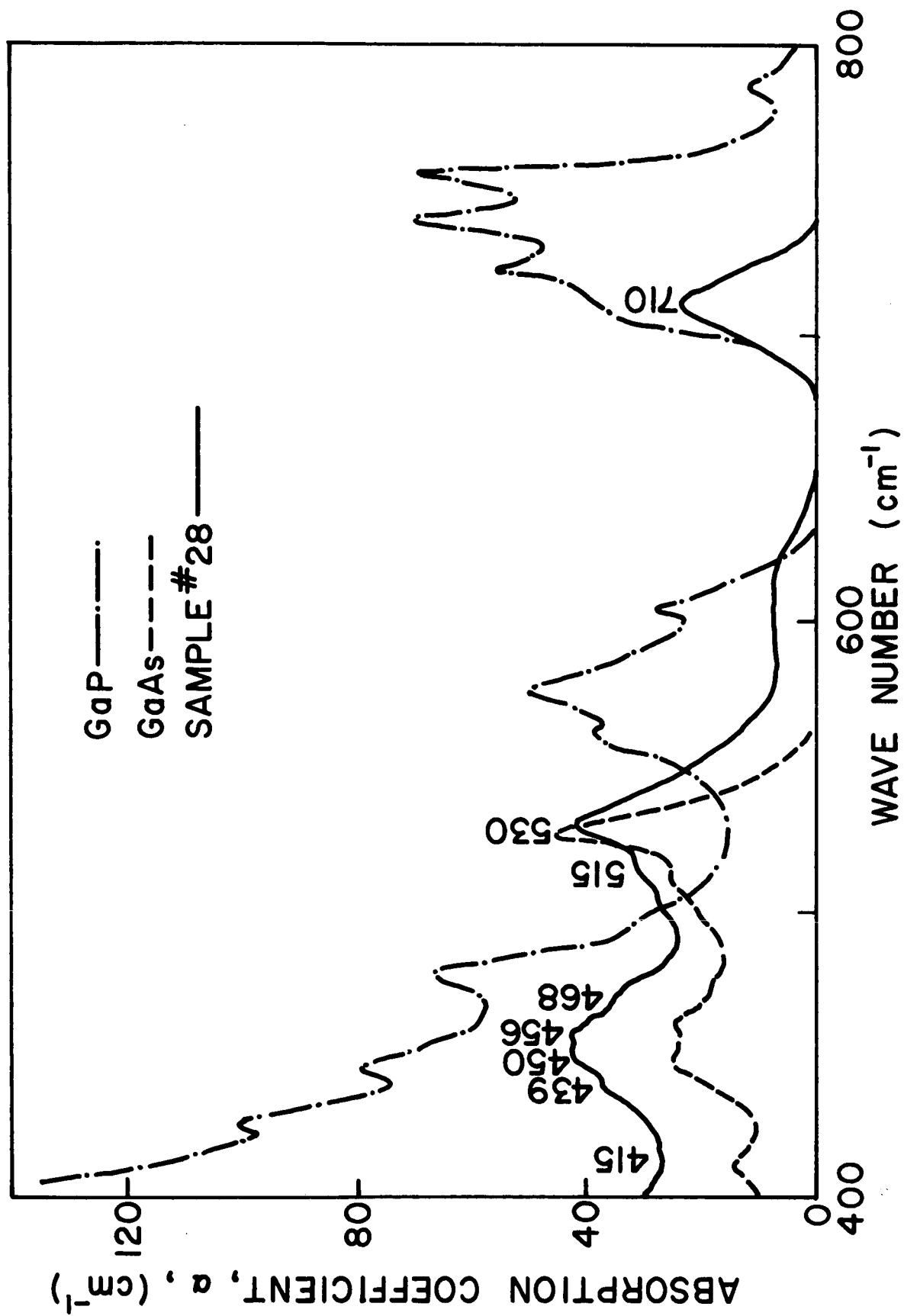


FIG.2

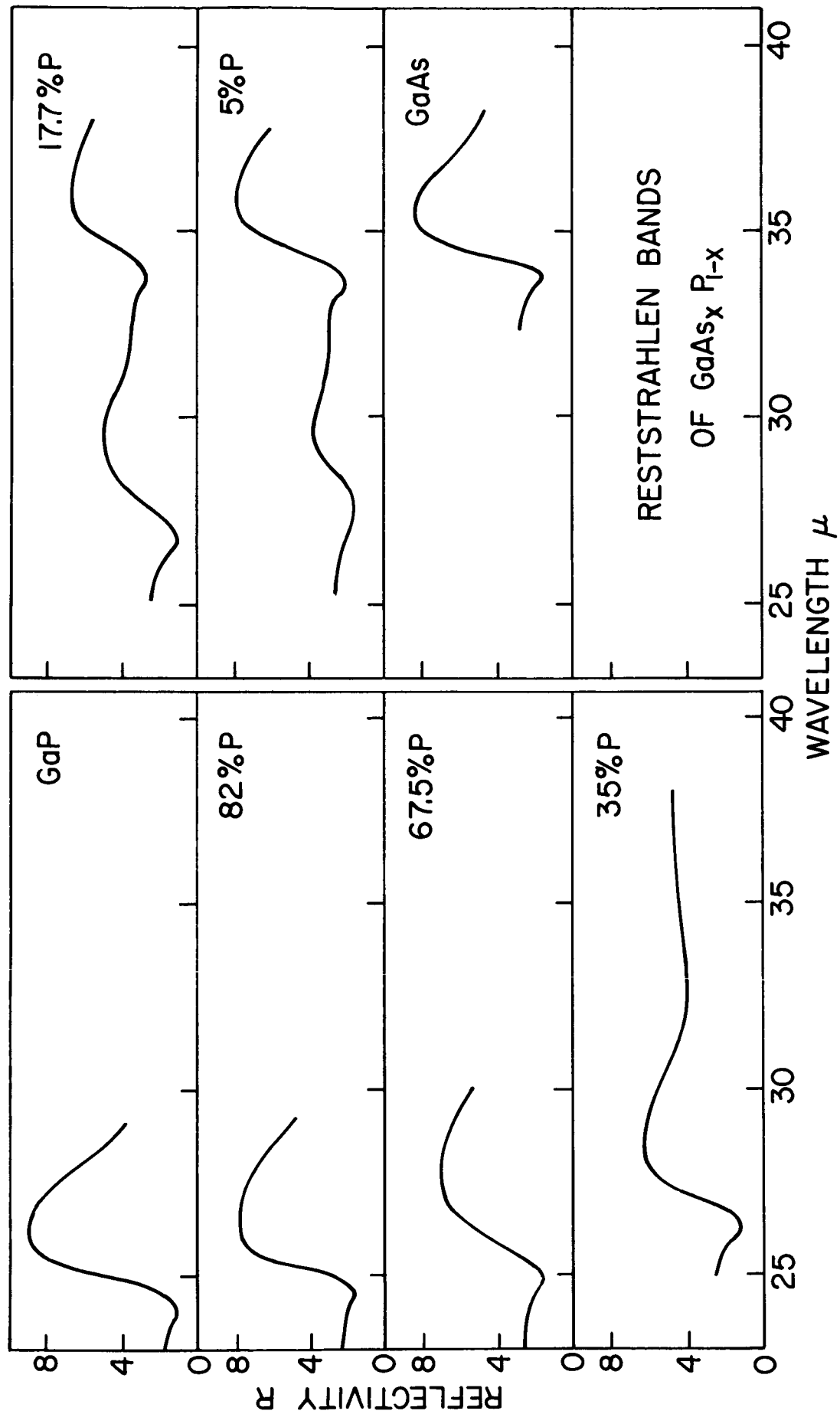


FIG. 3

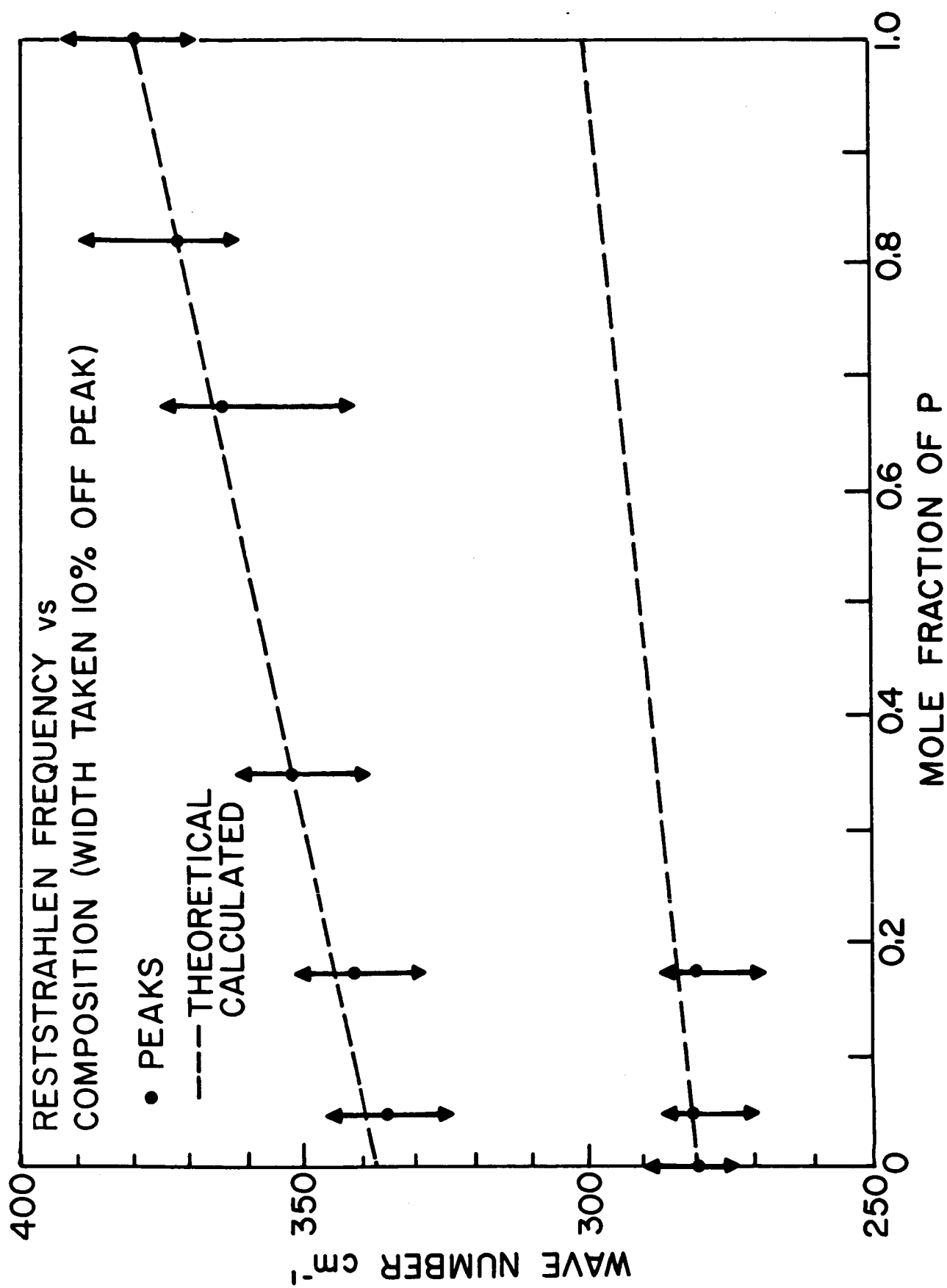


FIG. 4